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H. W. Casey

D. J. Krupcale

THE EFFECT OF CERTAIN CHEMICAL TREATMENTS ON PHOTOLYTIC IMAGE FORMATION

Prepared by: H. W. Casey
D. J. Krupcale

Rochester Institute of Technology

Evening College

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The Effect of Certain Chemical Treatments on Photolytic Image Formation

H. W. Casey, D. J. Krupcale

R.I.T. Evening College

Rochester, New York

A study of certain chemical baths and combinations of chemical baths was made to determine their effect on the print-out image of a specially-prepared conventional developing-out enlarging paper. These print-out images were formed and made visible entirely from the photolytic effect of the image exposure. Arc lamp, tungsten lamp and electronic flash lamp exposures were made; arc lamp exposures were the most satisfactory. The chemical associated with the most image improvement was stannous chloride.

Introduction

Yoshitada Tomoda has presented a paper[1] in which print-out effect was studied in a manner similar to the one presented here. Tomoda's experiment, although primarily directed at the possibility of measurement of gamma radiation for dosimetry, employed conventional tungsten light sensitometry for screening preliminary results.

Tomoda's treatments were made on a motion picture positive film. The film was bathed in dilute, single chemical solutions, and dried with ethanol. Tungsten lamp wedge attenuated exposures were made, and the resulting images were read using a conventional transmission densitometer.

1. Yoshitada Tomoda, "Enhancement of Print-Out Effect by Bathing Treatment," Phot. Sci. Eng., **5**: 226 - 229 (1961).

In Tomoda's work, five types of chemical reagents were used: metal salts, sulphur compounds, nitrogen compounds, organic reducing agents and organic acids. Silver nitrate produced the best result of the metal salts used; sodium sulfite, the best of the sulphur compounds; and triethanolamine and sodium nitrite, the best of the nitrogen compounds. Of the organic reducing agents, hydroquinone, metol, and catechol produced excellent results. Of the organic acids, none tested produced good results.

This paper presents an extension of Tomoda's work. Tomoda's most successful treatments are reproduced to determine their effectiveness on a photographic paper. In addition, certain pre-treatments are made in an attempt to produce further improvement in print-out effect by chemical interaction. These pre-treatments are intended to chemically and/or physically alter the basic emulsion, thereby giving the second treatment a different environment in which to work.

These chemicals are expected to directly produce, or provide the environment for succeeding treatments to ultimately produce, the following characteristics: halogen acceptance, high pH, low pAg, crystal rupture or faulting, and ion mobility in the emulsion.

Preliminary tests of several photographic paper products for print-out effect with and without treatment, showed Du Pont "Warmtone" distinctly superior to the others tested. Du Pont "Warmtone" is chloro-bromide projection speed enlarging paper with a fine grain structure. Du Pont "Warmtone" was used exclusively in the following experiment.

Experimental Procedure

The experiment was designed around nine chemicals, four classified as pre-reagents, four classified as reagents and one classified as a humectant. As a control, water was added to each classification as one of the chemicals. Each chemical was tested alone; each pre-reagent was tested with each reagent; the humectant was tested with each chemical and each reagent pre-reagent combination.

TABLE I. Experiment Design

Without Humectant

Reagent / Pre-Reagent	1 Water	2 Phenidone	3 Na_2SO_3	4 $Na\ NO_2$	5 $Ag\ NO_3$
1 Water	11	12	13	14	15
2 Cu Cl	21	22	23	24	25
3 TEA	31	32	33	34	35
4 $Cd\ I_2$	41	42	43	44	45
5 $Sn\ CI_2$	51	52	53	54	55

With Humectant

Reagent / Pre-Reagent	6 Water	7 Phenidone	8 $Na_2\ SO_3$	9 $Na\ NO_2$	10 $Ag\ NO_3$
6 Water	16	17	18	19	110
7 Cu Cl	26	27	28	29	210
8 TEA	36	37	38	39	310
9 $Cd\ I_2$	46	47	48	49	410
10 $Sn\ CI_2$	56	57	58	59	510

The basic sensitized material used for testing (Du Pont "Warmtone" Y) was a fine grain, double weight, medium speed projection paper. In order to provide a more primitive emulsion and avoid as much as possible any unknown reaction, the samples were washed in ethanol for five minutes, then washed in running tap water for four hours. These treatments removed any ethanol soluble sensitizing dye and other possible organic emulsion additives, and any emulsion water soluble salts.

The chemicals used were all A.C.S. Specification Reagent Grade, except Phenidone B and sugar (sucrose). These were photo grade chemicals. In solution preparation, all chemicals were prepared at 2X concentration and diluted before use. All the chemicals dissolved readily in distilled water except cuprous chloride and Phenidone B. The cuprous chloride was dissolved in a 3 per cent hydrochloric acid solution and the Phenidone B was dissolved in a 2 per cent potassium hydroxide solution.

TABLE II. Concentration of the chemicals ready-for-use

Pre-Reagents	%	Reagents	%	Humectant	%
Cuprous Chloride	0.10	Phenidone B	0.5	Sucrose	20.0
Triethanolamine	3.0	Sodium Sulfite	1.0		
Cadmium Iodide	3.0	Sodium Nitrite	3.0		
Stannous Chloride	5.0	Silver Nitrate	1.0		

All bathing treatments were done in photographic trays. The treatment duration was five minutes, and fresh solution was used for each test with a dissimilar history. All handling was done under amber safelights. The chronological order of the separate experiment operations is given below in Figure 1.

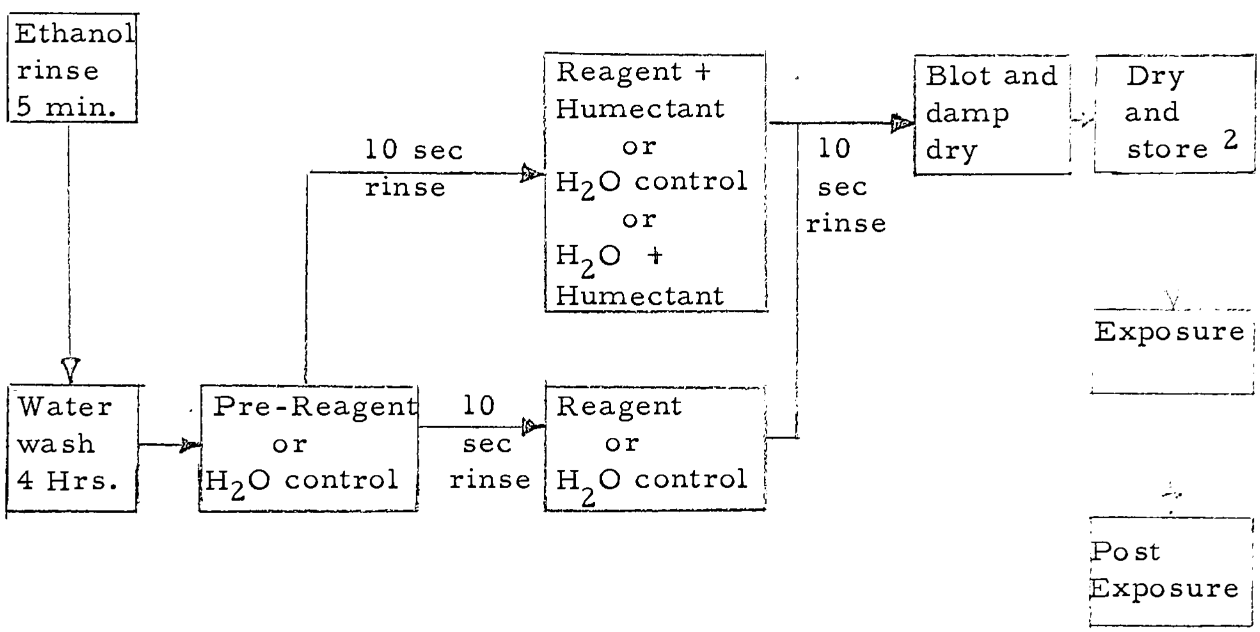

Figure 1. Flow diagram.

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2. Samples from the individual treatments were held in black photographic envelopes two weeks before initiating the exposure phase of the experiment.

Wedge attenuated exposures were made in a vacuum frame on the treated samples using arc lamps, tungsten lamps and electronic flash lamps. Following the wedge exposure, the samples were:

1. Further treated with unattenuated General Electric Cool White fluorescent lamps for 16 hours at 50 foot candles;

2. Exposed for six seconds to UV light (four - 8 watt BLB fluorescent lamps at 6 inches) while being held at 230°F;

3. Not treated further.

Lamp	Color Temp.	Exposure	Dis-tance	Wedge	Lamp Characteristics
Arc	6500°K	2 min. @ 5000FC	6 ft.	$\sqrt{2}$	95 amp White Flame
Tungsten	3400°K	2 min. @ 2500FC	6 ft.	$\sqrt{2}$	PAR- 38 Flood
Flash	approx. 6000°K	1/1000 sec. 2-200 watt sec.	1 ft.	$\sqrt{2}$	Hershey Studio Lamps (2)

Figure 2. Exposure.

The resulting sample densities were read with a Welch Densichron Reflection Densitometer; the lamp voltage was reduced from 6.3 to 4.5 volts to retard sample photolyzation during reading. The D-max and D-min of each test were recorded, together with their respective step number.[3] Densities were read using a porcelain secondary reflectance standard based on magnesium carbonate as 100% reflectance.

Visual impressions of the color of the image, the speed, the image quality, and the image stability were recorded.

3. The step number associated with D-max was the lowest step number on which D-max occurred; with D-min it was the highest step number on which D-min occurred.

Contrasts of the samples were determined mathematically[4] from the D-max, D-min and their respective step numbers. From these three variables, a single factor, "Enhancement Value," was derived. The formula for Enhancement makes D-max and D-min of equal importance and contrast one-half as important. The factors determining contrast are also partly dependent upon D-max and D-min. The relative importance of D-max decreases logarithmically as D-max increases. This means that a given increase in D-max is more important when the D-max is low than when it is high. The same is true of contrast, and the converse is true of D-min.

$$\text{Enhancement Value} = \text{Log}\left[\frac{100.\,(\text{D-max.})}{100.\,(\text{D-min.})}\right] + \left[\frac{[\log 100.\,(\text{contrast})] - 1}{3}\right]$$

Using this value, contingent on proper weighting, the tests were evaluated and compared by a single measure of the improvement that the various treatments produced. It also reduces the data to a form easily handled by Duncan's multiple range test.[5]

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4. Contrast = $\frac{\Delta D}{\Delta \text{LogE}}$ where ΔD = D-max — D-min, and Δ LogE = the difference between D-max and D-min step numbers multiplied by .15 (wedge density step incrementation)

5. Li, Introduction to Statistical Inference, Edward Brothers, Inc., Ann Arbor, 1957, p. 238.

Because the wedge exposure and subsequent treatment were not considered important in the evaluation of chemicals tested, the exposure and further treatment, which yielded the best results, was used to evaluate the test chemicals. Of the fifty different tests selected, however, all but five were tests with arc lamp image (wedge) exposures without further light treatment (Figure 2.). (None of the tests was improved as a result of post exposure except the cadmium iodide-Phenidone and the cadmium iodide-sodium sulfite tests.)

RESULTS

Quantitative Evaluation

In an array of the fifteen best results[6], the cadmium iodide-silver nitrate treatment and the stannous chloride - Phenidone - sugar treatment comprised the first significant group.

Stannous chloride was the pre-reagent used in eight of the first fifteen best results. Triethanolamine occurred four times, the control (water) twice and cadmium iodide once.

Individual Effect of Chemicals:

Within the parameters of the experiment, positive results were shown by six individual chemicals. In decreasing order of enhancement value they are:

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6. See Appendix, Table IV, Array of fifteen best Enhancement Values.

RESULTS (cont'd)

1. Stannous chloride
2. Cuprous chloride
3. Sodium sulfite
4. Sodium nitrite
5. Silver nitrate
6. Triethanolamine

(The effects of cuprous chloride, sodium sulfite, sodium nitrite, silver nitrate and triethanolamine were not significantly different.)

No effect or negative results were found with the other individual chemicals.

Effect of Humectant:

The humectant had little effect on any of the tests.

Effect of Chemical Combinations:

With cadmium iodide pre-reagent treatment, significant improvements by interaction were shown, in decreasing order of enhancement value, by silver nitrate, Phenidone and sodium sulfite.

With stannous chloride, significant improvements were shown, in decreasing order of enhancement value, by Phenidone and sodium sulfite. Sodium nitrite and silver nitrate gave negative results.

With triethanolamine, significant improvements were shown, in decreasing order of enhancement value, by sodium nitrite and sodium sulfite. Silver nitrate and Phenidone produced negative results.

With cuprous chloride, none of the reagents used showed any significant improvement. Negative results were found with silver nitrate and sodium sulfite.

Qualitative Evaluation

Subjective evaluation of the experiment samples for color showed that all produced acceptable, although varied, colors. Specific colors associated with specific chemical treatments, as well as physical quality[7] evaluation, are shown below in Table III.

TABLE III. Subjective evaluation of pre-reagents and reagents

Chemical	Background Color	Image Density Tone	Quality
Cuprous chloride	buff	purple	good
Triethanolamine	tan	red-brown	good
Cadmium iodide	yellow	pale blue	poor
Stannous chloride	buff	brown	excellent
Phenidone	yellow	yellow-brown	fair
Sodium sulfite	buff	purple-brown	good
Sodium nitrite	buff	red-brown	good
Silver nitrate	buff	purple-brown	poor

The subjective evaluation is parallel to the Enhancement evaluation except for sample treatments with silver nitrate. Silver nitrate treatment produced almost uniformly negative subjective results.

7. Mottle, stain or other visual irregularity.

Discussion

Other areas of investigation might include:

1. Optimization of chemical concentrations. Only one concentration of each chemical (plus control) was used in this experiment.

2. Other chemicals and/or combinations of chemicals to be investigated, particularly other stannous salts, other organic reducing agents, or other cuprous salts.

3. A different basic emulsion containing all chloride or iodo-chloride or iodo-bromide.

4. Other methods of treatment such as chemical addition during emulsion preparation, or spray or vapor application after preparation.

5. A different exposure media such as X-radiation.

In the evaluation of a printing-out sensitized material, certain characteristics not within the scope of this experiment could be of interest.

1. The reciprocity characteristics could be evaluated. A desirable characteristic of printing out emulsions is a high level of low intensity reciprocity failure. This characteristic provides greater safelight latitude and extends the useful life of the print under normal viewing illumination.

2. With some printing out materials, the high-intensity-formed image can be enhanced by an overall post exposure to low intensity light[8]. The factors effecting this "light-developability" could be studied.

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8. Heman D. Hunt, "High Speed Direct-Recording Papers," Phot. Sci. Eng., 5:104-108 (1961)

APPENDIX

TABLE IV

Array of the fifteen best enhancement values[9]

	Pre-reagent	Reagent	Humectant
1	Cadmium iodide -	Silver nitrate	none
2	Stannous chloride -	Phenidone	Sucrose
3	Stannous chloride -	Sodium sulfite	none
4	Stannous chloride -	Phenidone	none
5	Stannous chloride -	Sodium sulfite	Sucrose
6	Stannous chloride -	Control (water)	none
7	Stannous chloride -	Control (water)	Sucrose
8	Control (water) -	Sodium nitrite	Sucrose
9	Stannous chloride -	Sodium nitrite	Sucrose
10	Triethanolamine -	Sodium nitrite	none
11	Triethanolamine -	Sodium sulfite	Sucrose
12	Stannous chloride -	Sodium nitrite	none
13	Triethanolamine -	Sodium nitrite	Sucrose
14	Triethanolamine -	Phenidone	Sucrose
15	Control (water) -	Sodium nitrite	none

9. Array is in decreasing order of enhancement value.

APPENDIX

TABLE V

RAW DATA - ENHANCEMENT VALUES

Humectant →	None				
Reagent →	Water	Phenidone	Na_2SO_3	$NaNO_2$	$AgNO_3$
Pre-Reagent ↓					
Water	0.777 0.801	0.237 0.257	0.800 0.805	1.004 1.114	0.890 0.896
CuCl	0.926 0.936	0.838 0.850	0.805 0.813	0.885 0.902	0.795 0.795
Triethanolamine	0.911 0.931	0.331 0.347	0.986 0.986	1.052 1.063	0.586 0.593
CdI_2	-0.330 -0.330	0.547 0.565	0.329 0.371	-0.330 -0.330	1.336 1.339
$SnCl_2$	1.177 1.180	1.210 1.222	1.237 1.246	1.016 1.033	0.844 0.852

Humectant →	Sucrose				
Reagent →	Water	Phenidone	Na_2SO_3	$NaNO_2$	$AgNO_3$
Pre-Reagent ↓					
Water	0.854 0.874	0.363 0.383	0.908 0.913	1.089 1.096	0.754 0.754
CuCl	0.673 0.708	0.900 0.922	0.824 0.844	0.901 0.901	0.808 0.808
Triethanolamine	1.009 1.018	0.320 0.320	1.037 1.051	1.009 1.020	0.448 0.462
CdI_2	-0.330 -0.330	0.771 0.785	0.586 0.607	-0.330 -0.330	0.861 0.878
$SnCl_2$	1.166 1.152	1.311 1.306	1.198 1.215	1.068 1.085	-0.330 -0.330